

Design criteria of a chemical reactor based on a chaotic flow

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We consider the design criteria of a chemical mixing device based on a chaotic flow, with an emphasis on the steady-state devices. The merit of a reactor, defined as the Q -factor, is related to the physical dimension of the device and the molecular diffusivity of the reactants through the local Lyapunov exponents of the flow. The local Lyapunov exponent can be calculated for any given flow field and it can also be measured in experimental situations. Easy-to-compute formulae are provided to estimate the Q -factor given either the exact spatial dependence of the local Lyapunov exponent or its probability distribution function. The requirements for optimization are made precise in the context of local Lyapunov exponents.

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I. INTRODUCTION

A major concern in chemical engineering is to react two or more species to form a new chemical product [1]. To increase production, one could boost the reaction rate by a catalyst which is an optimization on a microscopic level. One could also carry the reactants by a flow and maximize the diffusive effect that brings the chemicals together to react. Traditionally the flow is designed to be turbulent to achieve higher mixing effect. Started in the 1980s, non-turbulent but chaotic flows, are advocated to achieve the same effect with significantly less energy consumption in driving the flow [2,3]. Much work has been done in this area [4–7], but some of the fundamental issues on optimizing the design still require a clarification. This paper intends to report some progresses along this line. The emphasis on the local Lyapunov exponent of the flow and its role in *quantitatively* determining the physics of both advective ‘mixing’ and diffusive transport, is an unique aspect of this investigation.

The typical reaction is a three species event, chemical A reacts with chemical B to form chemical C ,



The quantities of interest are the concentrations or number densities of each species, C_A, C_B , and C_C . The concentration of the end product is not independent and can be expressed in terms of the history of C_A and C_B . If the chemicals are carried by a flow, the mathematical model for the mixing-reaction process is the advection-diffusion-reaction equation. Written out explicitly for each species, they are

$$\partial C_A / \partial t + \mathbf{v} \cdot \nabla C_A = \nabla \cdot (D \nabla C_A) - \kappa C_A C_B; \quad (1)$$

$$\partial C_B / \partial t + \mathbf{v} \cdot \nabla C_B = \nabla \cdot (D \nabla C_B) - \kappa C_A C_B. \quad (2)$$

In the general case, the chemicals react according to $mA + nB \rightarrow lC$. The concentrations in equations (1,2) should then be replaced by the scaled concentrations $C'_A \equiv C_A/m$, $C'_B \equiv C_B/n$, and $C'_C \equiv C_C/l$.

We will assume that the original carrier flow is sufficiently energetic that the back-reaction of the reaction process on the background flow is negligible. This assumption decouples the third governing equation, for example, the Navier-Stokes equation for the flow field, from the two coupled advection-diffusion-reaction equations (1,2). The principles for the design optimization, are then found by solving the advection-diffusion-reaction equations and identifying the flow features that crucially affect the production rate and quality.

The underlying physics is better explained by a transformation of the variables of the original advection-diffusion-reaction equations. Define $\phi \equiv C_A - C_B$ and $f \equiv C_A + C_B$, one has

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$$\partial\phi/\partial t + \mathbf{v} \cdot \nabla\phi = \nabla \cdot (D\nabla\phi), \quad (3)$$

$$\partial f/\partial t + \mathbf{v} \cdot \nabla f = \nabla \cdot (D\nabla f) - \frac{1}{2}\kappa(f^2 - \phi^2). \quad (4)$$

Obviously $f^2 - \phi^2 = 4C_A C_B \geq 0$ and $f \geq \|\phi\|$.

There are generally two classes of reactors, which we will call a closed flow system and an open flow system. A canonical closed flow system is a stirred tank [10]. Mathematically it corresponds to an initial value problem, with simple boundary conditions. The degree of mixing is measured over time. A canonical open flow system is a tubular device such as an automobile catalytic converter. Raw exhaust gas constantly flows in, the poisonous elements are removed by chemical reactions, and the treated gas is discharged to the tail pipe. The system is expected to function in steady state. Mathematically it is a time-independent boundary value problem. The integral form of equations (3,4) makes the global balance transparent. For an engineering device operating in steady state,

$$\int_V \frac{\partial f}{\partial t} d^3\mathbf{x} = \frac{\partial}{\partial t} \int_V f d^3\mathbf{x} = 0.$$

The remaining part is

$$\int [f\mathbf{v} - D\nabla f] \cdot d\mathbf{a} = -\frac{1}{2}\kappa \int_V (f^2 - \phi^2) d^3\mathbf{x}.$$

Here we have assumed incompressibility $\nabla \cdot \mathbf{v} = 0$ for mathematical simplicity. The left hand side is the rate of new reactant influx and the right hand side is the rate of reactant depletion due to reaction. Naturally for a steady state device they balance each other out.

The fast reaction scenario would further reduce the mathematical complexity and help clarifying the basic issues. If the chemical reaction rate is sufficiently fast that

$$\kappa \gg -\frac{\int [f\mathbf{v} - D\nabla f] \cdot d\mathbf{a}}{\int_V (f^2/2) d^3\mathbf{x}}, \quad (5)$$

then $f \approx \|\phi\|$ everywhere in the system since

$$\int_V [f^2 - \phi^2] d^3\mathbf{x} \ll \int_V f^2 d^3\mathbf{x}.$$

Mathematically that is to say that the reaction is fast so once ϕ is found, the problem is solved by setting $\|\phi\| = f$. Physically it says that two different reactants react so fast that they can not coexist at the same point anywhere in the device. Hence at least one of reactant densities has to vanish locally and $\|\phi(\mathbf{x})\| = f(\mathbf{x}) = \text{Max}(C_A, C_B)$. For engineering design purposes, the equivalent statement is that the reaction is sufficiently fast so that the efficiency of the reactor is determined by the efficiency of mixing. This is precisely the motivation for embedding the reactants into a turbulent flow and more recently a chaotic one. We note that the use of a catalyst is intended to boost the microscopic reaction rate κ .

As expected, the inequality in equation (5) is equivalent to the statement that the Damköhler number is much greater than the Peclet number. The Peclet number Pe is the ratio between the characteristic diffusion time L^2/D and the advective time scale L/U . The Damköhler number Da is the ratio between the characteristic diffusion time and the typical reaction time $1/\kappa\langle f/2 \rangle$ with $\langle \dots \rangle$ an average over space. A reaction is fast if the typical reaction time is much shorter than the advective time scale, *i.e.* $Da/Pe \gg 1$. Although in a closed flow system like a stirred tank the ratio Da/Pe might be less than one, it has to be greater, and usually much greater, than one in a working steady-state device. This is a trivial statement of the fact that the advective time scale L/U in a steady-state device is simply the duration for the reactants to stay in the reactor before discharge. It has to be longer than the reaction time. Otherwise even a perfectly mixed reactants at the inlet will not form much product at the time of discharge. In practice, the requirement for a ‘fast’ reaction $Da/Pe \gg 1$ is not difficult to accommodate. For example it can always be satisfied in a tubular device by simply increasing the longitudinal length L . Indeed, the minimum design constraint of a steady-state chemical reactor is to have the longitudinal Damköhler number greater, or much greater, than the longitudinal Peclet number. Here longitudinal refers to the streamwise direction.

The degree of global mixing in a reactor is measured by

$$\sigma(t) \equiv \frac{1}{2} \int_V \varphi^2 d^3\mathbf{x} \quad (6)$$

with

$$\varphi \equiv \phi - \int \phi d^3 \mathbf{x} / \int d^3 \mathbf{x}$$

The separation between reactants is always non-negative so $\sigma \geq 0$. The governing equation for the global mixing index is

$$\frac{d\sigma}{dt} = \mathcal{F} - \int D(\nabla\varphi)^2 d^3 \mathbf{x}.$$

The flux of separated chemicals into the system is

$$\mathcal{F} \equiv - \int \left[\frac{\varphi^2}{2} \mathbf{v} - D \nabla \frac{\varphi^2}{2} \right] \cdot d\mathbf{a}.$$

Now we can distinguish two kinds of mixing devices, closed and open, which correspond to an initial value problem and a time-independent boundary value problem respectively. For a closed system,

$$\mathcal{F} = 0, \quad d\sigma/dt = - \int D(\nabla\varphi)^2 d^3 \mathbf{x}.$$

Obviously

$$\sigma \geq 0 \longrightarrow \sigma = 0 \quad \text{for sufficiently long time.}$$

An open system is markedly different. For example \mathcal{F} normally is positive. It must be positive for steady state device where $d\sigma/dt = 0$. Pictorially speaking, separated chemicals are brought in, φ^2 non-zero where $\mathbf{v} \cdot d\mathbf{a} < 0$. Mixed and reacted chemicals are discharged, φ^2 essentially zero where $\mathbf{v} \cdot d\mathbf{a} > 0$.

The flow design is driven by the rate of $\sigma \rightarrow 0$ which measures the quality of the reactor. The desire for a background flow can be clearly illustrated in a closed system, where the relaxation of σ is completely due to diffusion driven by the gradients of φ . Since

$$(\nabla\varphi)^2 = \frac{\varphi^2}{l^2}$$

the relaxation time scale is l^2/D . If there is no convection, l is of reactor size and the relaxation time scale l^2/D is hopelessly long.

Towards a better reactor, the carrier flow must be designed to drive gradients in φ or ϕ , which is an ideal task for a chaotic flow. In addition, to achieve better quality of the end product, it is desired that the gradients are driven ‘uniformly.’ In the case of a chaotic flow, the size of the KAM islands should be minimized, which is an obvious direction for optimization. There is another, more subtle, issue concerning the non-uniformity of the chaoticity and the existence of a barrier to diffusion even within the chaotic region. This subtlety can not be resolved by the standard Poincare section technique, but it can be made mathematically precise in terms of the finite time or local Lyapunov exponents of a flow. The goal of this paper will be to explain how to understand the merit of a reactor by the finite time or local Lyapunov exponent of the carrier flow.

Our approach based on the local Lyapunov exponents should be contrasted with the past heavy reliance on the Poincare section as a diagnostic to measure the extent of mixing, an approach that is prone to misinterpretation and does not provide any rate information [5]. The limitation of the Poincare section technique was explicitly noted by Swanson and Ottino in [11], and prominently restated by Bryden and Brenner in [5]. Muzzio and Liu presented a numerical demonstration in a two dimensional mixing-reaction problem [6]. The local Lyapunov exponent analysis, in our view, complements the Poincare section by providing the exact rate information and removes the ambiguities associated with the Poincare plots.

The rest of the paper is organized as follows. Section II gives an introduction on how the finite time Lyapunov exponent enters the description of a chaotic flow and the passive scalar transport. Section III briefly describes the time-dependent solution to the advection-diffusion equation, the more detailed analysis can be found in [8] for the two dimensional case and [9] for the three dimensional case. The main body of the paper, which includes sections IV V VI VII VIII, deals with the practically attractive steady-state reactors. The main mathematical formulation has utilized cylindrical geometry and quasi-two-dimensional flows for clarity and convenience, although the most important concepts and results can be readily generalized. Section IX highlights the main points of the paper.

II. FINITE TIME LYAPUNOV EXPONENT AND A CHAOTIC FLOW

A chaotic flow is characterized by the exponential variations of neighboring streamlines. For example, the separation between neighboring fluid trajectories of a divergence-free, time-periodic two dimensional flow obeys

$$(dl)^2 = (d\vec{l}_0 \cdot \hat{\mathbf{e}})^2 \exp(2\lambda t) + (d\vec{l}_0 \cdot \hat{\mathbf{s}})^2 \exp(-2\lambda t), \quad (7)$$

with $\lambda \geq 0$. A flow is called chaotic if

$$\lambda^\infty \equiv \lim_{t \rightarrow \infty} \lambda > 0,$$

otherwise it is said to be integrable. We note that the laminar to turbulent transition is marked by the emergence of many scales for the velocity field. The integrable to non-integrable transition concerns the behavior of the fluid trajectories, not the spectrum of the velocity field. This is why the stochasticity of a chaotic flow is also called Lagrangian turbulence (Lagrangian trajectories), in analog with the usual Kolmogorov-type Eulerian turbulence (Eulerian flow field). As far as the theory of advection-diffusion equation concerns, a qualitative change in the solution of the equation occurs at the integrable-nonintegrable transition. This should be contrasted with the standard treatment that presumes a turbulent background flow.

What we mean by a qualitative change in the solution of the advection-diffusion equation can be made precise by the rate at which the gradients of passive scalar field grow before the diffusive relaxation dominates the solution. In an integrable flow, $\nabla\phi$ grows linearly in time. If the Lagrangian trajectories become chaotic, $\nabla\phi$ increases exponentially in time. The exponential rate is given by the finite time or local Lyapunov exponent $\lambda(\xi, t)$, which depends on both position and time. That is to say, the value of λ depends on where the fiducial trajectory initially starts and how long one is tracing the fiducial trajectory. The time and especially the spatial dependence of the finite time Lyapunov exponent define the essential characteristics of the passive scalar transport.

The effects of advection and diffusion can be most clearly seen in Lagrangian coordinates. The Lagrangian coordinates are defined by a one-to-one mapping between the initial position and the current position of a fluid element, which is found by integrating

$$d\mathbf{x}(\xi, t)/dt = \mathbf{v}(\mathbf{x}, t)$$

with the initial condition $\mathbf{x}(\xi, t = 0) = \xi$. The description of a physical phenomena is independent of the choice of the coordinate system. Both \mathbf{x} and ξ can provide the necessary coordinate system, the first is the usual Eulerian coordinates while the second one is the well-known Lagrangian coordinates. Unlike the usual Eulerian coordinates, the Lagrangian coordinates have a non-trivial metric tensor. In fact it has both a space and a time dependence. If the metric tensor of the Eulerian frame is the unit matrix, the metric tensor of the Lagrangian coordinates is defined as

$$g_{ij} \equiv \partial\mathbf{x}/\partial\xi^i \cdot \partial\mathbf{x}/\partial\xi^j \quad \text{and} \quad g^{ij} \equiv \nabla\xi^i \cdot \nabla\xi^j. \quad (8)$$

The metric tensor, by its definition, is entirely determined by the flow field. Even for a perfectly smooth steady flow field, the metric tensor tends to become singular as t becomes large. If the flow is integrable, the metric tensor diverges at most quadratically in time [9]. For a chaotic flow, the metric tensor blows up exponentially in some subspaces. As long as the flow field is well-behaved, the metric tensor is well behaved and does not possess any finite time singularity.

Since the Lagrangian coordinates are attached to the fluid elements, the solution to the ideal advection equation is equivalent to integrating the trajectory $\mathbf{x}(\xi, t)$ and setting $\phi(\mathbf{x}(\xi, t), t) = \phi(\xi, t = 0)$. If the spatial gradient of ϕ is written in Lagrangian coordinates,

$$[\nabla\phi(\mathbf{x}, t)]^2 = \nabla_0\phi(\xi) \cdot \vec{g} \cdot \nabla_0\phi(\xi),$$

the coordinate derivative in Lagrangian coordinates of ϕ , $\nabla_0\phi(\xi)$, would be time independent, *i.e.* given by initial condition, $\nabla\phi(\mathbf{x}, t = 0)$. When diffusion is included, $\phi(\xi, t)$ would have a time dependence, so does $\nabla_0\phi(\xi, t)$. Two important characteristics can be immediately explained once the covariant representation of the metric tensor, g_{ij} , is identified as the Oseledec matrix [12]. Since g_{ij} is a positive, definite symmetric matrix, it can be diagonalized with real eigenvectors and positive eigenvalues,

$$g_{ij} = \exp(2\lambda t)\hat{\mathbf{e}}\hat{\mathbf{e}} + \exp(-2\lambda t)\hat{\mathbf{s}}\hat{\mathbf{s}} \quad (9)$$

with $\lambda \geq 0$. The gradient of ϕ can be written in the form,

$$(\nabla\phi)^2 = (\nabla_0\phi \cdot \hat{\mathbf{e}})^2 \exp(-2\lambda t) + (\nabla_0\phi \cdot \hat{\mathbf{s}})^2 \exp(2\lambda t). \quad (10)$$

The metric tensor that enters the last calculation is its contravariant form g^{ij} , which is the exact matrix inverse of g_{ij} , hence $g^{ij} = \exp(-2\lambda t)\hat{\mathbf{e}}\hat{\mathbf{e}} + \exp(2\lambda t)\hat{\mathbf{s}}\hat{\mathbf{s}}$.

What immediately can be seen is that under ideal advection, the passive scalar gradient would blow up exponentially in time without bound since $\nabla_0\phi(\xi)$ is time-independent. This reflects the singular nature of the diffusion term as a perturbation to the ideal advection equation. The existence of a diffusion term, no matter how small D is, would eventually remove any gradient in ϕ . Since the metric tensor has an exponential factor, the diffusion responsible for the relaxation of $\nabla_0\phi(\xi, t)$ must have a super-exponential dependence in order to overcome the exponential factor in the metric tensor. The second note is that the diffusion is essentially one dimensional since the exponential growing term in the metric tensor is only in the one dimensional subspace defined by $\hat{\mathbf{s}}$.

III. TIME-DEPENDENT SOLUTION TO THE ADVECTION-DIFFUSION EQUATION

In this section we give an example for a bounded flow, *i.e.* a closed system. The open flow configuration, the main focus of this paper, is treated afterwards. A closed system corresponds to an initial value problem. The equation to solve is the advection-diffusion equation,

$$\partial\varphi/\partial t + \mathbf{v} \cdot \nabla\varphi = \nabla \cdot (D\nabla\varphi).$$

We have defined

$$\varphi \equiv \phi - \bar{\phi}, \quad \text{and} \quad \bar{\phi} = \int \phi d^3\mathbf{x}.$$

Transforming into Lagrangian coordinates,

$$(\partial\varphi/\partial t)_\xi = \nabla_0 \cdot (D\vec{g}\nabla_0\varphi).$$

The tensor diffusivity $\vec{D} \equiv D\vec{g}$ in diagonal form is

$$\vec{D} = De^{2\lambda t}\hat{\mathbf{s}}\hat{\mathbf{s}} + De^{-2\lambda t}\hat{\mathbf{e}}\hat{\mathbf{e}}. \quad (11)$$

We have restricted the discussion to a two dimensional flow. The three dimensional case is treated in [9].

The exponential anisotropy of the tensor diffusivity along different directions implies that the diffusive relaxation is determined by a one dimensional diffusion equation,

$$\partial\varphi/\partial t = \nabla_0 \cdot De^{2\lambda t}\hat{\mathbf{s}}\hat{\mathbf{s}} \cdot \nabla_0\varphi. \quad (12)$$

The usefulness of above formulation rests on the fact that $\hat{\mathbf{s}}$ converges exponentially to a time asymptotic limit $\hat{\mathbf{s}}_\infty(\xi)$. A time-independent vector field $\hat{\mathbf{s}}_\infty(\xi)$ allows the usual construction of a coordinate system that makes the calculation well-defined. Parameterizing distance along the $\hat{\mathbf{s}}$ line by a scalar field β , one has

$$\frac{\partial\varphi}{\partial t} = \frac{\partial}{\partial\beta} De^{2\lambda t} \frac{\partial\varphi}{\partial\beta}. \quad (13)$$

The exponential convergence rate of $\hat{\mathbf{s}}$ to $\hat{\mathbf{s}}_\infty$ implies that the calculation based on the time-asymptotic spatial coordinates is exponentially accurate.

The solution to the one dimensional diffusion equation is determined by two quantities. One is the fundamental time scale of the problem, the local Lyapunov time of the flow $1/\lambda$. The other is the dimensionless number $\Omega \equiv \lambda L^2/D$, which is the ratio between the characteristic diffusion time scale L^2/D and the Lyapunov time of the flow. If $\Omega \gg 1$ which is generally true due to the smallness of the molecular diffusivity, the scalar field undergoes a pure advection until time $t_a \equiv (\ln 2\Omega)/2\lambda$. The ideal advection increases the gradients of the passive scalar field (in Eulerian frame) by a factor of Ω . There is a rapid diffusive relaxation [super-exponential in $\partial\varphi(\xi, t)/\partial\beta$] which removes the gradients $\nabla\varphi(\mathbf{x}, t)$ during a short interval of a few Lyapunov time after t_a .

A clarification should be made on the definition of the Lyapunov time for passive scalar transport studies. To our knowledge, in the literature (for a review, see [4]), the Lyapunov time of a flow is uniformly associated with the stretch rate, *i.e.* the largest positive Lyapunov exponent of the flow. This is a misconception and the reason can be easily seen by examining equations (7,9,10, 11,12). The correct statement is that the most negative Lyapunov exponent $-\lambda$, *i.e.*

the convergence rate, defines the Lyapunov time $1/\lambda$ for the passive scalar transport. In the case of a two dimensional time-dependent divergence-free flow which happens to be the starting point of much of the existing literature, the positive Lyapunov exponent has the same magnitude as the negative one due to the constraint of area-preserving, so this distinction is not mathematically important despite its physical significance. However, in the more general case of a three dimensional flow or compressible flows, a correct understanding of this subtlety is necessary both physically and mathematically.

If the finite time Lyapunov exponent does not vary in space, then one has the ideal situation that the diffusive relaxation uniformly removes the gradients. Unfortunately the only flow that is known to have this property is purely hyperbolic. An example is the Arnold's cat map. Generic flows are non-hyperbolic and the finite time Lyapunov exponent has a peculiar spatial dependence. Roughly speaking, $\lambda(\xi, t)$ varies smoothly along the \hat{s} lines, which is required for equations (12,13) to be well-posed. The variation of $\lambda(\xi, t)$ across the \hat{s} lines is pathological: the gradient of $\lambda(\xi, t)$ in directions other than \hat{s}_∞ has an exponential dependence in time. The smoothness of λ along the \hat{s} lines permits the existence of a class of diffusion barrier in a chaotic region. The pathology of λ across the \hat{s}_∞ direction gives rise to the fractal-like transport in both space and time.

A crude estimate of the mixing process can be based on the probability distribution function of the finite time Lyapunov exponent. If the distribution function is an δ function centered at λ^∞ . The relaxation of $(\nabla\phi)^2$ follows a simple route. The gradient grows by a factor of Ω and is then removed during a Lyapunov time centered on time $t_a \equiv (\ln 2\Omega)/2\lambda$. Equivalently the global mixing index $\sigma(t)$ stays the same until time t_a , after which it exponentially decays to zero within a few Lyapunov time. If the finite time Lyapunov exponent has a broadened distribution like that shown in [8], the time evolution of the global mixing index can be found by convoluting the ideal mixing curve with the λ distribution function. For a flow having noticeable amount of remnant integrable region, there is usually a significant bump at the left end of the distribution function. Since the distribution function is sampled over the entire space, there are actually two types of trajectories which could contribute to this bump. The first is simply the integrable trajectory lying on the KAM surfaces. The second one forms the so-called stochastic layer, a sticky region surrounding the remnant KAM islands. The bump in the distribution function is responsible for the long tail of the σ relaxation curve. The experimental observation of a spread in σ relaxation is determined by the λ profile.

Although the features of the global solution is roughly given by the mean Lyapunov time, the Ω number associated with the local Lyapunov time dictates the local details of the solution. For example, since diffusion occurs only along an \hat{s} line, the place with a peculiarly small finite time Lyapunov exponent would pose as a practical diffusion barrier. A more precise description is based on the theory of finite time Lyapunov exponent [8,13]. The finite time Lyapunov exponent exponentially converges to a form of three parts:

$$\lambda(\xi, t) = \frac{\tilde{\lambda}}{t} + \frac{f}{\sqrt{t}} + \lambda^\infty. \quad (14)$$

The two convergence functions have entirely different properties. The function $\tilde{\lambda}$ is a smooth function of space and it is related to the geometry of the \hat{s} line by

$$\hat{s}_\infty(\xi) \cdot \nabla_0 \tilde{\lambda} + \nabla_0 \cdot \hat{s}_\infty = 0. \quad (15)$$

The function $f(\xi, t)$ reflects the pathology in the spatial variation of the finite time Lyapunov exponent. First it does not vary along the \hat{s} direction,

$$\hat{s}_\infty \cdot \nabla_0 f(\xi, t) = 0. \quad (16)$$

Secondly it develops an exponentially growing gradients in the direction across the \hat{s}_∞ , for example,

$$\hat{e}_\infty \cdot \nabla_0 f \sim \exp(\lambda t).$$

Of course, the time dependence of $f(\xi, t)$ has to be bounded by \sqrt{t} so $\lim_{t \rightarrow \infty} \lambda = \lambda^\infty$.

Although equation (15) states that the finite time Lyapunov exponent achieves an extreme when $\nabla \cdot \hat{s}_\infty$ vanishes, numerical calculations show that λ reaches its local minimum where the \hat{s} line makes sharp bend. The sharp drop in the magnitude of λ implies that these sharp bends of an \hat{s} line are practical diffusion barriers. We note that an \hat{s} line belongs to a chaotic region, and they persist even if the flow is far from integrable. Equivalently speaking, even if the flow is driven globally chaotic without discernible KAM islands, there are still regions with retarded mixing. Since the production of new chemical C depends on the final diffusive relaxation of A and B, these diffusion barriers directly affects the quality of a reactor.

IV. STEADY STATE MIXER

An efficient engineering device employs an open flow operating at steady state. The simplest geometry for such a device is a pipe [7,14,15] so we will consider the cylindrical geometry. The flow field is assumed to be divergence-free and quasi-two-dimensional,

$$\mathbf{v}(x, y, z) = \hat{\mathbf{z}} \times \nabla \psi(x, y, z) + v_z(x, y) \hat{\mathbf{z}}. \quad (17)$$

The absence of a z dependence in $v_z(x, y)$ implies that the flow field is divergence-free in the transverse plane, $\nabla_{xy} \cdot \mathbf{v}_{xy}(x, y, z) = 0$ with $\mathbf{v}_{xy} = \hat{\mathbf{z}} \times \nabla \psi(x, y, z)$. If the mixer is operated at steady state ($\partial \phi / \partial t = 0$), the governing equation is

$$v_z \frac{\partial \phi}{\partial z} + \mathbf{v}_{xy} \cdot \nabla_{xy} \phi = \nabla_{xy} \cdot D \nabla_{xy} \phi + \frac{\partial}{\partial z} D \frac{\partial}{\partial z} \phi. \quad (18)$$

We have separated the divergence of the diffusive flux into longitudinal and transversal components. For an operating reactor, the longitudinal component becomes exponentially smaller than the transversal component going downstream before the onset of diffusive pulse that removes the transversal gradients. In the usual case that D is small and $R^2 v_z / LD \gg 1$, the longitudinal diffusion term is negligible so

$$v_z \frac{\partial \phi}{\partial z} + \mathbf{v}_{xy} \cdot \nabla_{xy} \phi = \nabla_{xy} \cdot D \nabla_{xy} \phi. \quad (19)$$

Here R is the radius of the cylinder and L is the total longitudinal length of the device.

The in-fluxes of reactants A and B are

$$\mathcal{F}_{A,B} \equiv \int v_z(x, y, z=0) C_{A,B}(x, y, z=0) dx dy.$$

The flux for each chemical can be defined for any cross section in the reactor, but only their difference is important. The differential flux of the reactants

$$F(z) = \int v_z(x, y) \phi(x, y, z) dx dy = \int v_z(x, y) (C_A - C_B) dx dy$$

is a constant in the longitudinal direction,

$$dF(z)/dz = \int v_z \frac{\partial \phi(x, y, z)}{\partial z} dx dy = 0.$$

For practical applications, an initial input is proper if $F(z=0) = 0$. The degree of mixing at the transversal plane is given by

$$\sigma(z) = \frac{1}{2} \int v_z(x, y) \phi^2(x, y, z) dx dy. \quad (20)$$

This spatially dependent mixing index $\sigma(z)$ should be distinguished from the global mixing index $\sigma(t)$ defined in equation (6). The reactants become better mixed as they go downstream. The rate of mixing is determined by the diffusive effect,

$$\frac{d\sigma}{dz} = - \int D \nabla_{xy} \phi \cdot \nabla_{xy} \phi dx dy. \quad (21)$$

The percentage of the chemicals failed to react is roughly measured by

$$\mathcal{R} = \frac{\sigma(z=L)}{\sigma(z=0)}.$$

The quality of the mixer(reactor) is measured by the Q -factor

$$Q \equiv \frac{1}{\mathcal{R}} = \frac{\sigma(z=0)}{\sigma(z=L)}.$$

In the impractical limit of $L \rightarrow \infty$ the chemicals would react completely for a proper initial input $F(z = 0) = 0$ and the Q -factor is infinite. For a finite L , the Q -factor is generally finite as well. For an intake flux

$$\mathcal{F}_A = \int v_z(z = 0) C_A dx dy,$$

the amount that does not react is about

$$\mathcal{F}_A / \sqrt{Q}.$$

If Q is infinite, the output of the final product is

$$O_C = \int v_z(x, y, z = L) C_C(x, y, z = L) dx dy = \mathcal{F}_A.$$

Otherwise

$$O_C \approx (1 - Q^{-1/2}) \mathcal{F}_A.$$

The optimization of a mixing device or a reactor is primarily looking for a balance between the production rate \mathcal{F}_A , reactor length L , and the desired Q -factor. Implicitly through the Q -factor there is also an energy consumption penalty (power P) for driving a flow field $\mathbf{v}(\mathbf{x})$. These correspond to four design constraints: 1] geometrical constraint, i.e. the physical size limit for the device; 2] production rate constraint; 3] production quality constraint; 4] energy constraint. The first three are kinematic constraints since they are uniquely determined by the flow field [Except that in a reactor, there is a minimal length constraint due to the finite reaction time, *i.e.* the system size has to be greater than $v_z/\kappa\langle f/2 \rangle$. This point was made earlier in the introduction]. The last one is a dynamical constraint and it requires solving the Navier-Stokes equation to relate the driving term to the flow field.

This paper addresses the kinematic constraints. The dynamical constraint for the flow field is more case-dependent. Nevertheless, a general statement can be made that it is usually less energy consuming to produce a smooth, non-turbulent, but chaotic flow, than a turbulent one. In the case of a tubular device, this is reflected by a small increase in the pressure drop over the tube, or equivalently the pumping power, to induce a chaotic flow with satisfactory mixing properties [16].

The physical meaning of the kinematic constraints will become clear once the solution to equation (18) is found. The most important property of the flow field in determining the kinematic constraint is the so-called local Lyapunov exponent, just like the time-dependent initial value problem. Instead of time, the z coordinate will be used to parameterize a fluid trajectory. The only constraint for z to be a good scalar for parameterization is that v_z nowhere vanishes. This is naturally satisfied in our choice of a quasi-two-dimensional flow field, $\partial v_z / \partial z = 0$. Any point satisfying $v_z(x_0, y_0) = 0$ would imply that v_z vanishes along a straight line from $(x_0, y_0, z = 0)$ to $(x_0, y_0, z = L)$, which strictly prohibits transport. Hence v_z would be made nonzero in a working device. This is easily achievable by an infinitesimal longitudinal perturbation.

The singular nature of the solution to the equation (19) can be seen by a coordinate transformation. The fluid trajectory is now parameterized by z and given by

$$\frac{dx}{dz} = \frac{v_x(x, y, z)}{v_z(x, y)}, \quad \frac{dy}{dz} = \frac{v_y(x, y, z)}{v_z(x, y)}. \quad (22)$$

For an arbitrary initial position (x_0, y_0) at $z = 0$ plane, a trajectory of the fluid element can be traced to (x, y) at z -plane. The functional relationship between $x(x_0, y_0, z)$ and $y(x_0, y_0, z)$ is found by integrating equation (22) with initial position (x_0, y_0) from $z = 0$ to z .

If the mixing equation is transformed into the (x_0, y_0) coordinates, one has

$$\left(\frac{\partial \phi}{\partial z} \right)_{x_0, y_0} = \frac{1}{v_z(x(x_0, y_0, z), y(x_0, y_0, z))} \nabla_{x_0 y_0} \cdot D \vec{g} \nabla_{x_0 y_0} \phi(x_0, y_0, z). \quad (23)$$

The metric tensor of the (x_0, y_0) coordinate, \vec{g} , has two forms, covariant and contravariant. The contravariant form is defined as

$$g^{ij} = \begin{pmatrix} \nabla x_0 \cdot \nabla x_0 & \nabla x_0 \cdot \nabla y_0 \\ \nabla x_0 \cdot \nabla y_0 & \nabla y_0 \cdot \nabla y_0 \end{pmatrix}$$

The covariant representation is given by

$$g_{ij} = \begin{pmatrix} \frac{\partial(x,y)}{\partial x_0} \cdot \frac{\partial(x,y)}{\partial x_0} & \frac{\partial(x,y)}{\partial x_0} \cdot \frac{\partial(x,y)}{\partial y_0} \\ \frac{\partial(x,y)}{\partial x_0} \cdot \frac{\partial(x,y)}{\partial y_0} & \frac{\partial(x,y)}{\partial y_0} \cdot \frac{\partial(x,y)}{\partial y_0} \end{pmatrix}$$

The metric tensor is a positive, definite matrix, so it can be diagonalized with positive eigenvalues and real eigenvectors. If the covariant form is written as

$$g_{ij} = \exp(2\eta z)\hat{\mathbf{e}}\hat{\mathbf{e}} + \exp(-2\eta z)\hat{\mathbf{s}}\hat{\mathbf{s}} \quad (24)$$

with $\eta \geq 0$, the contravariant form is

$$g^{ij} = \exp(-2\eta z)\hat{\mathbf{e}}\hat{\mathbf{e}} + \exp(2\eta z)\hat{\mathbf{s}}\hat{\mathbf{s}}, \quad (25)$$

since g_{ij} and g^{ij} are matrix inverse of each other. The meaning of $\hat{\mathbf{e}}$ and $\hat{\mathbf{s}}$ can be made precise by following the distance between neighboring two points,

$$(dx)^2 + (dy)^2 = [dx_0, dy_0]g_{ij}[dx_0, dy_0]^T.$$

Hence two initial points separating along the $\hat{\mathbf{e}}$ direction would diverge exponentially going downstream, but they would converge exponentially going downstream if their initial separation is along the $\hat{\mathbf{s}}$ direction. Conventionally $\hat{\mathbf{e}}$ is called the unstable direction and $\hat{\mathbf{s}}$ is the stable direction. The function $\eta(x_0, y_0, z)$ which depends on the initial position of the trajectory (x_0, y_0) and the longitudinal ending point z , is a local Lyapunov exponent measuring the exponential separation rate. The inverse of $\eta(x_0, y_0, z)$ defines a local Lyapunov scale, *i.e.* the longitudinal distance over which the separation of neighboring trajectories varies by one e-fold. This is also the longitudinal distance over which the gradient of a passive scalar field increases by one e-fold in the absence of diffusion.

The mixing-reaction process is easier to understand if one transforms equation (21) into the (x_0, y_0) coordinates,

$$\frac{d\sigma(z)}{dz} = - \int D \nabla_{x_0 y_0} \phi(x_0, y_0, z) \cdot \vec{g} \cdot \nabla_{x_0 y_0} \phi(x_0, y_0, z) J dx_0 dy_0.$$

The Jacobian of the (x_0, y_0) coordinates is identically unity if v_{xy} is divergence-free. Substituting the diagonal form of the metric tensor, equation (25), into above equation, one obtains

$$\begin{aligned} \frac{d\sigma(z)}{dz} = & - \int D \{ [\hat{\mathbf{s}}(x_0, y_0, z) \cdot \nabla_{x_0 y_0} \phi(x_0, y_0, z)]^2 \exp(2\eta z) \\ & + [\hat{\mathbf{e}}(x_0, y_0, z) \cdot \nabla_{x_0 y_0} \phi(x_0, y_0, z)]^2 \exp(-2\eta z) \} dx_0 dy_0. \end{aligned} \quad (26)$$

The reduction in $\sigma(z)$ can be calculated using a simpler form in the usual case $R^2 v_z \eta / D \gg 1$. The simplification comes from two factors: 1] the diffusive flux is negligible for small z , 2] $\hat{\mathbf{s}}(x_0, y_0, z)$ exponentially loses its z dependence, *i.e.* $\hat{\mathbf{s}}(x_0, y_0, z)$ can be replaced by its z -asymptotic limit $\hat{\mathbf{s}}_\infty(x_0, y_0)$ with an exponentially small correction. Combining these, one can calculate the mixing rate with exponential accuracy by

$$\frac{d\sigma(z)}{dz} = - \int D [\hat{\mathbf{s}}(x_0, y_0) \cdot \nabla_{x_0 y_0} \phi(x_0, y_0, z)]^2 \exp(2\eta z) dx_0 dy_0. \quad (27)$$

The gradient of $\phi(x_0, y_0, z)$ in the (x_0, y_0) coordinates is found by solving a simplified form of equation (23)

$$\left(\frac{\partial \phi}{\partial z} \right)_{x_0, y_0} = \frac{1}{v_z(x_0, y_0, z)} \frac{\partial}{\partial \beta} D e^{2\eta(x_0, y_0, z)z} \frac{\partial}{\partial \beta} \phi(x_0, y_0, z). \quad (28)$$

The β coordinate is defined by a parameterization along the $\hat{\mathbf{s}}$ lines

$$d\mathbf{x}_0 / d\beta \propto \hat{\mathbf{s}}_\infty(x_0, y_0) \quad \text{with} \quad \mathbf{x}_0 = (x_0, y_0).$$

The solution of this one dimensional equation differs from that of the full equation by an exponentially small term in z . The discrepancy is negligible if $R^2 v_z \eta / D \gg 1$ and the initial gradient has a scale comparable to R .

The solution to equations (27,28) has remarkable properties for a chaotic flow ($\eta > 0$.) Since the longitudinal distance plays the role of time in a steady state system, the usual characteristic diffusion time R^2/D gives rise to an equivalent characteristic longitudinal length for diffusion $R^2 v_z / D$. The ratio of this characteristic longitudinal length for diffusion and the Lyapunov length defines Ω ,

$$\Omega \equiv \frac{R^2 v_z \eta}{D}, \quad (29)$$

a dimensionless number that is typically much greater than one.

V. DEGREE OF MIXING VERSUS LONGITUDINAL LENGTH

Recall that the transversal mixing index $\sigma(z)$ is defined as

$$\sigma(z) \equiv \int \frac{1}{2} \phi^2(x, y, z) dx dy.$$

The variation of σ downstream is given by

$$\frac{d\sigma(z)}{dz} = - \int D \nabla \phi(x, y, z) \cdot \nabla \phi(x, y, z) dx dy.$$

σ is a monotonically decreasing function which corresponds to the time-irreversibility of the diffusion process. Dividing above equation by $\sigma(0)$ leads to a dimensionless form

$$\frac{1}{\sigma(0)} \frac{d\sigma(z)}{dz} = - \frac{2 \int D \nabla \phi(x, y, z) \cdot \nabla \phi(x, y, z) dx dy}{\int v_z(x, y, z=0) \phi^2(x, y, z=0) dx dy}.$$

In the case that η is a constant,

$$\frac{1}{\sigma(0)} \frac{d\sigma(z)}{dz} = - \frac{D}{v_z R^2} \exp\left[-\frac{e^{2\eta z} - 1}{2\Omega} + 2\eta z\right]. \quad (30)$$

Equation (30) can be integrated for an exact analytic expression,

$$\frac{\sigma(z)}{\sigma(0)} = \exp\left[-\frac{e^{2\eta z} - 1}{2\Omega}\right] \quad (31)$$

with Ω defined in equation (29). This is a remarkable expression that is best interpreted in the units of Lyapunov length. There is little mixing and hence reaction in a region within a critical length

$$L_c = \ln(2\Omega)/2\eta \quad (32)$$

from the intake of the device. In fact, there is only one e -fold drop in $\sigma(z)/\sigma(0)$ over the entire longitudinal length L_c ,

$$\frac{\sigma(L_c)}{\sigma(0)} = e^{-1}.$$

Each additional Lyapunov length beyond L_c produces a super-exponential jump in the production quality, e.g. at a length $L_c + N/\eta$,

$$\frac{\sigma(L_c + N/\eta)}{\sigma(0)} = \exp[-e^N],$$

thus a reactor of longitudinal length $L_c + N/\eta$ has a Q -factor of

$$Q = \exp[e^N]. \quad (33)$$

The above formula implies that it takes less than $N = 3$ additional Lyapunov lengths to achieve a Q -factor of 10^8 . For a reactor with a length of $L_c + 3/\eta$, less than one part of ten thousands input reactants fails to react at the moment of discharge. It must be emphasized that L_c is a modest number even if the reactants are extremely difficult to mix, which is usually the case due to the smallness of D . For example, even if $\Omega = 10^{10}$, L_c is about 12 Lyapunov length $1/\eta$. A reactor of Q -factor 10^{10} requires a total longitudinal length of 15 Lyapunov lengths. In giving out these numbers, we have assumed that the chemicals undergo a diffusion-limited reaction. Even if the reaction rate is so slow that L_c is less than a typical reaction length $v_z/\kappa\langle f/2 \rangle$, an additional longitudinal length of a reaction length in the engineering design would provide the extra room to achieve the desired Q -factor.

The assumption that η is a constant, is a deceptively nontrivial one. In actuality it implies a much more stringent topological constraint. It is known that only purely hyperbolic system can have a constant Lyapunov exponent, the canonical example being the Arnold's cat map. A point is hyperbolic if its stable and unstable directions are not degenerate. Generic systems such as hamiltonian flows, are not purely hyperbolic. In fact, we suspect that a diffeomorphism higher than C^2 would generally have nonhyperbolic points. In the case of hamiltonian systems, remnant KAM tori are one manifestation of the nonhyperbolicity. Points on the chaotic set can also be nonhyperbolic. In hamiltonian systems, they are responsible for the sharp bending of the \hat{s} lines.

VI. LOCAL LYAPUNOV EXPONENT AND THE Q -FACTOR

The local Lyapunov exponent, or equivalently the local Lyapunov length, has a profound role in determining the quality of a reactor. In retrospect, the design of a quality reactor can be considered as an optimization of the local Lyapunov exponents. The simplest way to understand the effect of a spatially varying Lyapunov exponent on mixing is through its probability distribution function $P(\eta, z = L)$ for a steady state reactor. If η is a global constant, $P(\eta, z = L)$ would, of course, be a delta function. Nonhyperbolicity prevents this for a generic flow. Instead there is a large spread in the distribution function. The mixing index, or the Q -factor, can be approximated by convoluting the distribution function with equation (31). For a device of longitudinal length L operating with reactants of characteristic diffusion time scale R^2/D , there is a critical Lyapunov exponent $\eta_c(z = L)$ given by the solution to equation

$$L = \frac{1}{2\eta_c(L)} \ln \frac{2v_z R^2 \eta_c(L)}{D}. \quad (34)$$

As long as

$$\eta_c(L) > \eta^T(L) \quad \text{with} \quad \eta^T(z = L) \equiv \frac{De}{2v_z R^2},$$

the proportion of the input reactants that fails to react is roughly given by

$$\int_0^{\eta_c(L)} P(\eta, z = L) d\eta,$$

assuming that $P(\eta, z = L)$ is normalized

$$\int_0^\infty P(\eta, z = L) d\eta = 1.$$

A crude estimate for the Q -factor of the reactor is then

$$Q = 1 / \int_0^{\eta_c(L)} P(\eta, z = L) d\eta. \quad (35)$$

The second critical Lyapunov length $\eta^T(z = L) \equiv De/2v_z R^2$ is determined by

$$\frac{\partial L_c(\eta)}{\partial \eta} \bigg|_{\eta=\eta^T(z=L)} = 0.$$

L_c is a monotonically decreasing function in η if $\eta > \eta^T$, but a monotonically increasing function if $\eta < \eta^T$. The longer the characteristic diffusion time R^2/D , the less likely that the second critical scale $\eta^T(z = L)$ plays a role. In other words, unless R^2/D is small enough to render the chaotic mixer unnecessary, one does not need to worry about the subtleties associated with η^T .

In the language of hamiltonian mechanics, the integrable region or the KAM surfaces, are absolute barriers to advective transport because no trajectories could cross them, at least for systems with no Arnold diffusion. It is also an effective barrier for diffusive transport in the advection-diffusion theory. This is explained by the time dependence of the largest eigenvalue of the metric tensor. It was shown [9] that the largest eigenvalue of the metric tensor in an integrable region grows at most quadratically in time, with the prefactor given by the shear rate of the surface [9], *i.e.* the derivative of the rotational transform normal to a KAM surface. Contrasted with the exponential growth in a chaotic region, the effective diffusivity in (x_0, y_0) coordinates, Dg^{ij} , is small and hence the diffusive relaxation occurs on a much longer time scale.

The simplest design optimization is to reduce the size of the remnant integrable regions. Once resonant perturbations are present, global stochasticity can be achieved by increasing the perturbation strength. This is remarkable since it separates the global stochasticity for the trajectories from the spectrum of the velocity field. A turbulent flow field is usually associated with a broad spectrum of the velocity field. A laminar, but chaotic, flow has well-behaved velocity field, which is reflected by a few isolated spectral peaks. The optimization involves the adjustment of the relative strength of the peaks. The reduction of the integrable regions can then be realized under the constraint of maintaining the laminar nature of the flow.

The signature of a significant amount of integrable region in the local Lyapunov exponent is a large bump at the near-zero end of the distribution function. The local Lyapunov exponent is also well-defined using the metric tensor in an integrable region, even though the asymptotic Lyapunov exponent vanishes. This is trivially explained by the fact that a quadratic function can always be approximated by an exponential function locally.

VII. GEOMETRICAL CONSTRAINT ON A PRACTICAL DIFFUSION BARRIER

Even if the integrable regions are so small that they are all invisible to naked eyes, or in the extreme, of size smaller than $\sqrt{DL/v_z}$, the local Lyapunov exponent still has a finite spread in the distribution function. What makes the matter worse is that the distribution function tends to preserve an asymmetry biased towards the small η end. This statement is based on equations (14,15,16) and the numerical observation that η always takes a local minimum, rather than a local maximum, where the \hat{s} line makes a sharp bend. Since the local Lyapunov exponent varies little where the \hat{s} line is straight, but makes a sharp dip when the \hat{s} makes a sharp bend, there is an overall bias towards small η in the distribution function, even if only the chaotic trajectories are included in the distribution function calculation.

Surprisingly the presence of a small local Lyapunov exponent does not always lead to a practical diffusion barrier. To be a practical diffusion barrier, not only a small effective diffusivity is required, but also the size of the structure. Roughly speaking, the diffusivity D sets the minimal size of a practical diffusion barrier, although the integrability of the trajectories also plays an important role. In an integrable region, the \hat{s} lines closes on itself forming closed KAM curves. The shear-induced fast diffusion is confined within the KAM surfaces so the radial diffusivity is just D . The minimal size requirement of a practical barrier is given by

$$w = \sqrt{DL/v_z}. \quad (36)$$

It is the mean spread of an initial δ -distribution at the center of an integrable island at the time of discharge.

In a chaotic region, diffusion occurs only along the \hat{s} direction, but the \hat{s} lines can not close on themselves. A single \hat{s} line indeed fills an entire ergodic component densely. The previous estimate for the integrable case, equation (36), usually is too small. The minimal size for the diffusion barrier is comparable to

$$w^2 = \int_0^L D \exp(2\eta z) v_z^{-1} dz.$$

The exact integration requires an exact form for η , and the results are much more difficult to interpret. We will use an idealized simple form for η to illustrate some of subtleties. Noting the empirical result that $\eta \propto -(\ln \kappa)/z$ [8] with κ the curvature of the \hat{s} line bend, we prescribe

$$\eta = \eta_c - (c_0 \ln \kappa)/z,$$

with the understanding that κ is scaled by $1/R$ and hence dimensionless. Combining with equation (34), one finds

$$w = R/\kappa^{c_0}. \quad (37)$$

This expression is not valid for large enough κ that $\eta = \eta_c - (c_0 \ln \kappa)/z$ approaching zero. That gives the lowest bound $w \sim \sqrt{D/v_z \eta_c}$, consistent with the worst scenario predicted by equation (36). Otherwise, equation (37) gives a minimal barrier width estimate that depends on the sharpness of the bends.

The quantity that w should be compared with, is the size of the region having a significantly smaller local Lyapunov exponent. This region can be estimated as follows [8]. The position (x_0^c, y_0^c) with a local minimum for η is solved from

$$\kappa_e(x_0^c, y_0^c) = 0 \quad \text{and} \quad \nabla_{x_0 y_0} \cdot \kappa_e(x_0^c, y_0^c) > 0,$$

where κ_e is the curvature of the \hat{e} line

$$\kappa_e \equiv \hat{e}_\infty \cdot \nabla_0 \hat{e}_\infty = -(\nabla_{x_0 y_0} \cdot \hat{s}_\infty) \hat{s}_\infty.$$

The core of the diffusion barrier is approximately bounded by the curve satisfying

$$\nabla_{x_0 y_0} \cdot \kappa_e(x_0^b, y_0^b) + \kappa_e^2(x_0^b, y_0^b) = 0.$$

(x_0^b, y_0^b) is the closest point from (x_0^c, y_0^c) satisfying the above constraint. Since the diffusion barrier is a sharp bend of an \hat{s} line, the width of the diffusion barrier is the inverse of the curvature at (x_0^b, y_0^b) , *i.e.* $1/\kappa_e(x_0^b, y_0^b)$. One conclusion can be drawn immediately. Those “diffusion barriers” with a size

$$1/\kappa_e(x_0^b, y_0^b) < \sqrt{DL/v_z} \quad (38)$$

are not practical diffusion barriers affecting the Q -factor of a reactor. A relaxed criteria is obtained by comparing $1/\kappa_e(x_0^b, y_0^b)$ with w in equation (37). This implies that the local geometry of the bends prohibits a simple resolution and explicit case-dependent calculation is required.

The cut-off size for a practical diffusion barrier brings a natural limit on the finest grid size in a numerical calculation. It also opens the possibility for a paradoxical statement that a smaller η in the distribution function might not imply poorer mixing because the geometrical constraint, equations (36,37). Consequently equation (35) might not be a proper estimate for a globally chaotic flow.

An appropriate formula for estimating the Q -factor is based on the exact spatial dependence of the local Lyapunov exponent, $\eta(x_0, y_0, L)$. The formula is based on the integral

$$\int \Theta(\eta^c - \eta(x_0, y_0, z)) dx_0 dy_0,$$

where $\Theta(x)$ is the step function

$$\Theta(x) = 0 \text{ for } x < 0; 1 \text{ for } x > 0.$$

The geometrical constraint, equation (38) or alike, is incorporated by imposing a fixed grid size of $\sqrt{DL/v_z}$ for calculating the above integral. Written in discrete form,

$$Q = \frac{Av_z}{DL \sum_i \sum_j \Pi(\eta^c - \eta(i, j, L))} \quad (39)$$

where A is the total area of the cross section and the summations are over all grid points on a cross section. In the case that $\Omega \gg 1$, $\sqrt{DL/v_z}$ can be tiny compared with the transversal scale of the device R . Equation (39) is the proper formula for calculating the Q -factor in a highly chaotic flow. It should also yield a better estimate for the near-integrable cases, but might not be necessary. In principle, if the flow field $\mathbf{v}(x, y, z)$ is known, one would calculate $\eta(x_0, y_0, L)$ and use equation (39) for Q . The main usage of a probability distribution function based formula like equation (35) is in experimental situations where an exact measurement of $\eta(x_0, y_0, L)$ is inaccessible. $P(\eta, z = L)$ can be easily approximated by a limited amount of measurements. For those who could afford the time and resources, all quantities can be found to exponential accuracy by solving equations (27,28) for a given velocity field $\mathbf{v}(x, y, z)$.

In retrospect, a fully chaotic reactor can be further optimized by balancing the value of the local Lyapunov exponent and the sharpness of the \hat{s} -bend. The basic idea is to either straight out the \hat{s} line or make the bends sufficiently sharp that equation (37) is violated.

VIII. A SPECIFIC NUMERICAL EXAMPLE

Since the goal of this paper is to demonstrate the basic principles rather than working with a specific device, the illustrative example will be chosen as simple as possible and computationally as efficient as possible. Nevertheless, there are a few features that we do intend to include to make it practically relevant. First we want the example flow to have a bounded chaotic region since it is supposed to be confined by a pipe. The flow is also expected to be stochastic along the axis. Divergence-free is another useful feature to be consistent with earlier analysis.

The simplest chaotic flow of the form equation (17) has v_z a constant and ψ a periodic function of z . The standard treatment of this class of flow is to construct a mapping by sampling at the period of ψ along z axis. The mapping thus generated preserves both the topology of the Lagrangian trajectories, the functional form of the local Lyapunov exponents (except z takes discrete values), and the geometry of the \hat{s} lines. Mapping is enormously more efficient than the flow in computations. Hence our example will employ a mapping directly, but with the understanding that it was reduced from a constant- v_z and z -periodic- ψ smooth three dimensional flow.

It should be noted right away that in a practical application, an analytic form of the flow field is unlikely available, let alone an exact reduction to a mapping. However, this simplification is just for the convenience of illustration, the lack of it does not prevent a practical calculation.

There are three equations mapping (x_n, y_n, z_n) to $(x_{n+1}, y_{n+1}, z_{n+1})$. One of them is simply

$$z_{n+1} = z_n + \Delta z$$

with Δz the period of ψ . To insure area conservation, the example mapping that relates (x_n, y_n) to (x_{n+1}, y_{n+1}) is defined by a generating function, which has one free parameter k ,

$$S(x_n, y_{n+1}) = x_n y_{n+1} + k \ln(1 + x_n^2 + y_{n+1}^2).$$

Here k signifies the perturbation. The map is given by

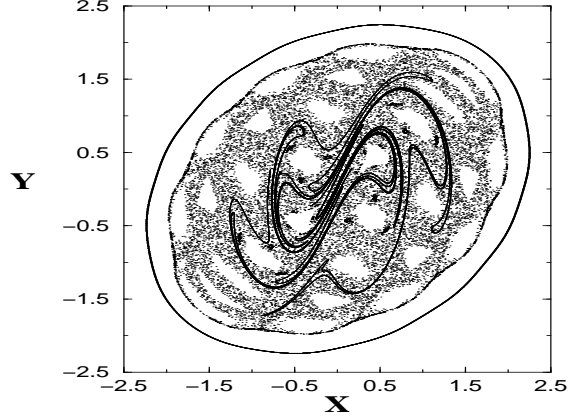


FIG. 1. Poincaré plot of the map given in equations (40,41) with $k = 1.4$. The solid line is an \hat{s} line on (x_0, y_0) plane.

$$x_{n+1} = \frac{\partial S}{\partial y_{n+1}} = x_n + 2k \frac{y_{n+1}}{1 + x_n^2 + y_{n+1}^2}; \quad (40)$$

$$y_n = \frac{\partial S}{\partial x_n} = y_{n+1} + 2k \frac{x_n}{1 + x_n^2 + y_{n+1}^2}. \quad (41)$$

For $k \ll 1$ this is the twist map with the angle of twist per iteration or every longitudinal advance of Δz , equal to $2k/(1 + x^2 + y^2)$. The map has a non-zero Lyapunov exponent near the axis, $x_n^2 + y_{n+1}^2 \ll 1$, if k is greater than unity.

This map is made explicit by solving a cubic equation for y_{n+1} in terms of x_n and y_n . To do this, define s so $y_{n+1} = s + y_n/3$, which implies $y_{n+1}^2 = s^2 + 2sy_n/3 + y_n^2/9$. One then finds

$$s - \frac{2}{3}y_n + \frac{2kx_n}{1 + x_n^2 + \frac{1}{9}y_n^2 + \frac{2}{3}sy_n + s^2} = 0,$$

which implies

$$s^3 + s(1 + x_n^2 + \frac{1}{9}y_n^2) - \frac{4}{9}sy_n^2 + 2kx_n - \frac{2}{3}y_n(1 + x_n^2 + \frac{1}{9}y_n^2) = 0.$$

Define

$$a = 1 + 1 + x_n^2 - \frac{1}{3}y_n^2 \quad \text{and} \quad b = 2kx_n - \frac{2}{3}y_n(1 + x_n^2 + \frac{1}{9}y_n^2).$$

The equation for s can then be written in the standard form for a cubic, $s^3 + as + b = 0$. This equation has a unique real root if

$$r^2 \equiv \left(\frac{b}{2}\right)^2 + \left(\frac{a}{3}\right)^3$$

is positive, the situation for this map. The real root of the cubic is then

$$s = \left(r - \frac{1}{2}\right)^{\frac{1}{3}} - \left(r + \frac{1}{2}b\right)^{\frac{1}{3}}.$$

It is straightforward to show that the map is stochastic near the axis for $k > 1$. Near the axis, $x_n^2 + y_{n+1}^2 \ll 1$, the map reduces to $y_{n+1} = y_n - 2kx_n$ and $x_{n+1} = x_n + 2ky_{n+1}$. This map is linear and can be solved by $x_n = x_0\Gamma^n$ and $y_n = y_0\Gamma^n$. One finds $(\Gamma - 1)y_0 = -2kx_0$ and $(\Gamma - 1)x_0 = 2k\Gamma y_0$ or $(\Gamma - 1)^2 + (2k)^2\Gamma = 0$. So

$$\Gamma = (1 - 2k^2) \pm 2\sqrt{k^2(k^2 - 1)}.$$

Since the map is area preserving the two roots must satisfy $\Gamma_+\Gamma_- = 1$. If $k > 1$, one of the roots, Γ_- , satisfies $\|\Gamma_-\| > 1$ and the map is stochastic with a Lyapunov exponent $\ln \|\Gamma_-\|$.

Figure 1 plots the intercepts of trajectories on the (x_0, y_0) plane. The topology of this intercepts tells the integrability of the trajectories going downstream. Since the flow field is periodic in z , the cross sections at $z = N\Delta z$ would have the same topology as that of (x_0, y_0) plane. Because of this, an efficient way to understand the topology is by projecting the intercepts of a long trajectory with cross sections at $z = N\Delta z, N = 0, 1, 2, \dots$, on the (x_0, y_0) plane. Since we already have the proper mapping, this becomes simply plotting the trajectories of the two dimensional mapping $(x_n, y_n) \rightarrow (x_{n+1}, y_{n+1})$. This is exactly how figure 1 is generated. Obviously our example map has a bounded chaotic region and it is stochastic near the axis.

The most important feature we wish to demonstrate here is the geometry of the \hat{s} lines and the spatial variation of the local Lyapunov exponent. The $\hat{s}(x_0, y_0)$ line sits on the $z = 0$ cross section. The statement that diffusive relaxation only occurs along the \hat{s} lines in (x_0, y_0) coordinates is equivalent to say that, initial chemical reactants located along an \hat{s} line will come close together and react to form new product C_C . The sharp bends of the \hat{s} line give rise to a peculiarly small local Lyapunov exponent which hinders diffusive relaxation. This relationship between the local Lyapunov exponent and the \hat{s} -bends is shown in Figure 2. Wherever the curvature of the \hat{s} goes up sharply, there is a significant dip in the local Lyapunov exponent.

IX. CONCLUSIONS

We have considered the design criteria of a chemical reactor device based on a chaotic flow. Particular attention has been paid to a steady state reactor, where the Lyapunov length provides the fundamental spatial scale for the problem. The advantages of a chaotic flow for a steady-state reactor can be summarized into two scaling relations: 1] the minimum longitudinal length of a reactor, L_c , has a logarithmic dependence on the diffusivity D , equation (32); 2] the quality of the reactor, the so-called Q -factor, has a super-exponential dependence on each additional Lyapunov length beyond L_c , equation (33).

The Lyapunov length $1/\eta$, as defined through equations (22, 24), is a local Lyapunov length since it depends on the initial position (x_0, y_0) and the longitudinal displacement z of the test fluid point. The local Lyapunov length are defined everywhere in the (x_0, y_0) plane, independent of whether the trajectory is chaotic or integrable. If the global flow field is known, the Q -factor of the reactor can be calculated via equation (39). In the experimental situation that the global flow field is not available, one can approximate the probability distribution function of the local Lyapunov exponent (length) by repeated measurements over time. The Q -factor can then be estimated by equation (35). Although the derivation is presented with the assumption that flow field obeys equation (17), these formulae are expected to be useful under more general conditions, such as a weak z -dependence of v_z and a weak time dependence of \mathbf{v} . The fast reaction scenario, equation (5), which brought mathematical simplicity to the discussion, can also be relaxed. A naive way to approach this is assuming that there is no reaction till length $L_c + N/\eta$, after which the reaction is suddenly turned on. If the fast reaction condition is satisfied, near-perfectly mixed chemicals A and B immediately react to form C . Otherwise there is a delay to achieve the same Q -factor. The additional length for the reactor is the reaction length, the product of the reaction time $1/\kappa\langle f/2 \rangle$ and the longitudinal flow velocity v_z .

For a closed flow reactor such as a stirred tank, the results obtained for the steady-state device can be straightforwardly translated by identifying the longitudinal length z as time t . The time scales replace the spatial scales as the quantities of concern. For example, the Lyapunov length $1/\eta$ is replaced by the Lyapunov time $1/\lambda$ and the critical length L_c is replaced by a critical advection time t_a . One difference is that in a steady-state tubular device, the streamwise distance can always be used to reduce the problem to a two dimensional one, equation (22), but the time-dependent closed flow reactor usually has to deal with a truly three dimensional flow, in addition to a possible time dependence. Fortunately, aside from some additional subtleties, the main physical characteristics of the transport of a passive scalar in a three dimensional flow is the same as the two dimensional case [9].

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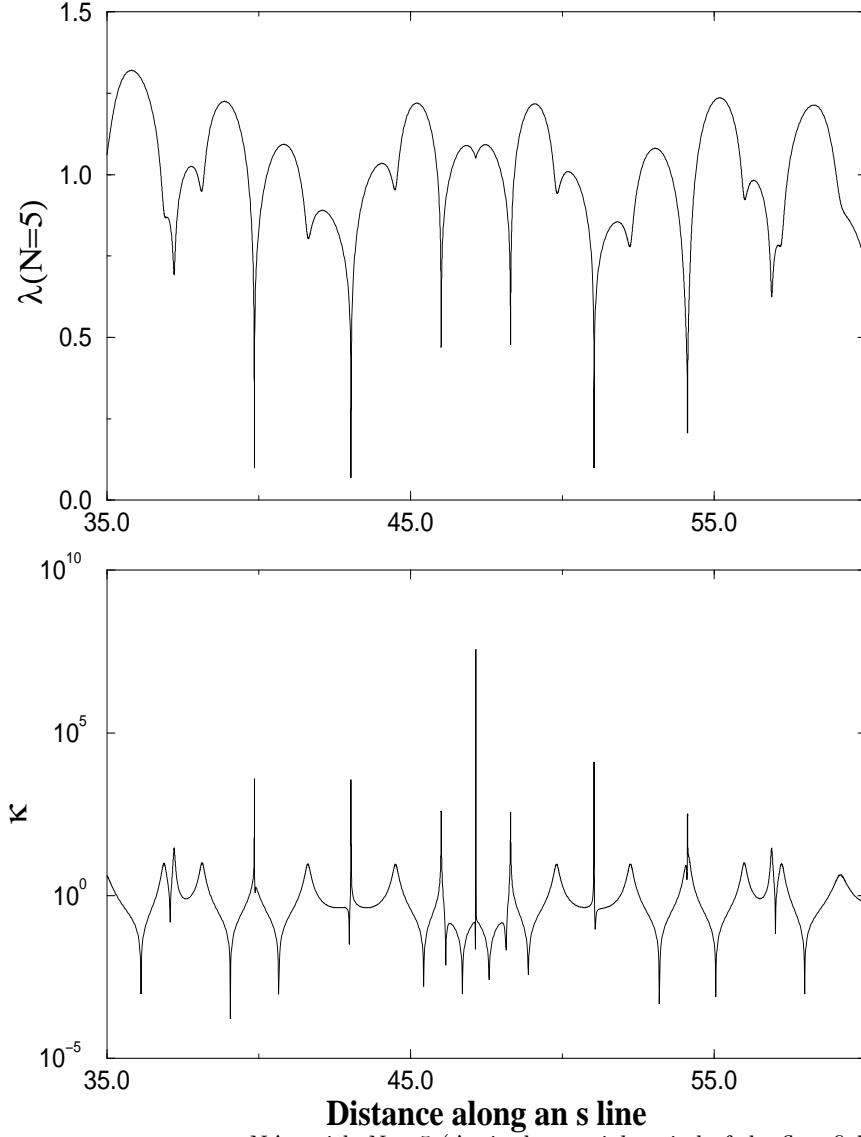


FIG. 2. The local Lyapunov exponent at $z = N\Delta z$ with $N = 5$ (Δz is the spatial period of the flow field in z direction) and the curvature κ of the \hat{s} line are plotted along an \hat{s} line shown in figure 1. The local Lyapunov exponent makes a sharp dip wherever the \hat{s} line makes a sharp turn. The missing dips at extremely large curvature are due to finite machine precision and integration stepsizes.

- [1] D.E. Rosner, *Transport Processes in Chemically Reacting Flow Systems* (Butterworths, Boston, 1986).
- [2] H. Aref, J. Fluid Mech. **143** (1984) 1.
- [3] J.M. Ottino, *The Kinematics of Mixing: Stretching, Chaos and Transport* (Cambridge University Press, Cambridge, 1989).
- [4] J.M. Ottino, Chem. Eng. Science **49** 24A (1994) 4005.
- [5] M.D. Bryden and H. Brenner, J. Fluid Mech. **325** (1996) 219.
- [6] F.J. Muzzio and M. Liu, Chem. Eng. J. **64** (1996) 117.
- [7] D.R. Sawyers, M. Sen, and H.-C. Chang, Chem. Eng. J. **64** (1996) 129.
- [8] X.Z. Tang and A.H. Boozer, Physica D **95** (1996) 283.
- [9] X.Z. Tang and A.H. Boozer, "Advection and diffusion in a three dimensional chaotic flow," preprint (1997).
- [10] G.B. Tatterson, *Scaledup and Design of Mixing Processes* (McGraw-Hill, New York, 1994).
- [11] P.D. Swanson and J.M. Ottino, J. Fluid. Mech. **213** (1990) 227.
- [12] J.-P. Eckmann and D. Ruelle, Rev. Mod. Phys. **57** (1985) 617.
- [13] X.Z. Tang and A.H. Boozer, Phys. Lett. A **236** (1997) 476.
- [14] W.R. Dean, Phil. Mag. J. Sci. **4** (1927) 319.
- [15] C.S. Lee, J.J. Ou, and S.H. Chen, Chem. Eng. Sci. **42** (1987) 2484.
- [16] N. Acharya, M. Sen, and H.-C. Chang, Int. J. Heat and Mass Transfer, **35** (1992) 2475.